

# Preliminary Published Application

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Title:

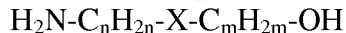
### Stripper for photo resists

The invention concerns stripping agents for photo resists based on

(a) an aprotic polar organic solvent and

(b) an organic base,

which contain as component (a) 45-65 wt.% of at least one of the compounds 1,3-dimethyl-2-imidazolidinone or 1,3-dimethyl tetrahydro-2-(1H)-pyrimidinone and as component (b) 55-35 wt.% of at least one compound of formula I



in which X signifies a single bond, O or NH, and  $n$ ,  $m$  denote the numbers 1 through 4.

## **Description**

The invention concerns new stripping agents for photoresists based on an aprotic polar organic solvent and an organic base.

The term photoresist is ordinarily used for organic polymer materials that can be structured by light and which are used in photolithographic processes and related fields of technology, e.g., in the production of printing plates, printed electric circuits and printed circuit boards or in microelectronics in the production of integrated semiconductor components.

In the production of integrated microelectronic semiconductor components, the semiconductor substrate material is coated with the photoresist; by exposing the photoresist film to an image and subsequently developing it, then positive or negative photoresist relief structures are obtained. The latter serve as templates for the actual structuring process on the semiconductor substrate, such as etching, doping, coating with metals, other semiconductor materials or even insulating materials. After this, the photoresist templates are usually removed. The circuit structures of the microchips are formed on the substrate by a large number of similar process cycles.

For the process steps of removing the photoresist from the substrate, special solvents -- in technical jargon called photoresist strippers -- are required which must satisfy a series of high requirements today. The primary prior condition for a usable stripper is that it must remove the photoresist rapidly and without residue from the substrate without attacking the substrate in so doing. At the same time it should operate sufficiently effectively even at low temperatures and in the case of necessity at a higher operating temperature, say in a case of photoresists that were secondarily dried at a high temperature, do not evaporate or are otherwise changed. The stripper should also be miscible with water in order to be rinsed off with water for purposes of process economy. Another essential requirement is that photoresist strippers today are practically only usable in industrial production processes if they can also be disposed of in a toxicologically unobjectionable and environmentally friendly manner or at least without problems.

The known strippers contain, for example, chlorinated hydrocarbons such as methylene chloride, polar organic solvents such as dimethyl formamide or N-methyl pyrrolidone, alkanolamines such as mono-, di-, or triethanolamine, glycol ethers and

esters such as ethylene glycol monoethyl ether or ethoxyethyl acetate, strong organic bases such as tetramethylammonium hydroxide, ketones such as acetone, methyl ethyl ketone or cyclohexanone, cyclic ethers such as tetrahydrofuran or dioxane or strong acids such as sulfuric acid-hydrogen peroxide mixtures.

From this representative survey of photoresist stripper components it is not difficult to see that practically all stripping agents produced from them represent only compromise solutions which cannot satisfy all of the current requirements in any way. Either the corresponding stripping agents are not sufficiently active at low temperatures so that bath temperatures of about 75°C or more are necessary, in which case problems arise due to evaporation or decomposition and through the attack of sensitive substrates, or mixtures that are more favorable from the application engineering standpoint contain toxic or at least toxicologically objectionable constituents. Strippers for photoresists are described in EP 219789, consisting of mixtures of water-soluble amino compounds and propylene glycol derivatives, such as mixtures of 2-(2-aminoethylamino)ethanol and tripropyleneglycol methyl ether, to which favorable application engineering properties are ascribed. Propylene glycol derivatives are presently considered to be less objectionable toxicologically than ethylene glycol derivatives. Despite this, a not inconsiderable risk potential must be ascribed to them because of the phototoxic effects found in animal experiments.

The invention therefore had the objective of developing new stripping agents for photoresists having high effectiveness and if possible not displaying the disadvantages of the known photoresist strippers.

Surprisingly it has now been found that strippers for photoresists based on

- (a) an aprotic polar organic solvent and
- (b) an organic base,

which contain as component (a) 45-65 wt.% of at least one of the compounds 1,3-dimethyl-2-imidazolidinone or 1,3-dimethyl tetrahydro-2-(1H)-pyrimidinone and as component (b) 55-35 wt.% of at least one compound of formula I



in which a single bond, O or NH and  $n$ ,  $m$  signify the numbers 1 to 4, are considerably superior in practically all essential criteria to the known photoresist strippers.

The object of the invention is therefore the above-characterized photoresist strippers.

The strippers according to the invention are qualitatively composed essentially of component (a), i.e. an aprotic polar organic solvent and component (b), i.e. an organic base. The well-known compounds 1,3-dimethyl-2-imidazolidinone and 1,3-dimethyltetrahydro-2-(1H)-pyrimidinone function as component (a). These compounds may be present individually or in a mixture in the stripper according to the invention. 1,3-dimethyl-2-imidazolidinone is especially preferred. Amino compounds of formula I function as component (b). Formula I represents alkanolamines, in which the alkylene group may also be interrupted by an oxygen atom or an NH group, with a total of 2-8 C atoms. The alkylene groups in this case may be straight-chained or also branched-chained. Typical compounds of formula I are ethanolamine, 3-amino-1-propanol, 3-amino-2-propanol, 2-(2-aminoethylamino)ethanol, 2-(2-aminoethoxy)ethanol. These compounds may also be present individually or in a mixture in the strippers according to the invention. 2-(2-aminoethylamino)ethanol is especially preferred as component (b). The strippers according to the invention have 45-65 wt.% of component (a) and 55-35 wt.% of component (b). Mixtures consisting of 50-63% component (a) and 50-40 wt.% component (b) are preferred, in which case component (a) is preferably 1,3-dimethyl-2-imidazolidinone and component (b) is preferably 2-(2-aminoethylamino)ethanol. A mixture of 52-wt.% 1,3-dimethyl-2-imidazolidinone and 48 wt.% 2-(2-aminoethylamino)ethanol represents an especially preferred variant of the stripper according to the invention.

According to the current state of knowledge, the strippers according to the invention as well as the constituents on which they are based are toxicologically unobjectionable, can therefore be handled without problem, and are easily disposed of. Furthermore, they are water-soluble or water-miscible and therefore satisfy the requirement of being capable of being completely rinsed off with water without residue.

The high efficacy of the strippers according to the invention is especially surprising. Even at low bath temperatures, say at room temperature, photoresists can be removed from the substrate without residue within a short time, typically 5-7 minutes. Photoresists that are known to be difficult to remove because of the high after-drying temperature, e.g., 180-200°C, can be removed without problem with the strippers

according to the invention at elevated bath temperatures, say between 75 and 150°C. The duration of the treatment in this case is typically between 3 and 6 minutes. They are considerably superior in their effect to the known photoresist strippers, especially those from EP 219789. The reason for this superior effectiveness may be seen in an unexpected synergistic effect of components (a) and (b) within the quantitative composition bandwidth according to the invention.

Because of the high boiling point, predominantly above 160 °C, of the constituents of the strippers according to the invention under ordinary process conditions practically no evaporation losses occur so that long standing times of the stripper baths are assured.

Sensitive substrates such as aluminum coatings are not attacked by the strippers according to the invention even after a long time and at elevated temperature.

The strippers according to the invention are suitable in principle for removing any organic polymer coatings. They are preferably used for removing photoresists from semiconductor substrates during production of microelectronic circuits, in which case practically all conventional photoresist materials come under consideration. Besides the preferred application with positive photoresists based on Novolac resins and photosensitive quinone diazide compounds they may also be used successfully with radiation-cross-linked polymer layers, such as those obtained with negative photoresists of conventional type and also in the case of photoresists on a polyimide basis. They can be applied by all of the current procedures such as the dip, spray or puddle process under the usual process conditions.

The toxicological unobjectionability and the excellent application-engineering properties make the stripper according to the invention a valuable enrichment in photoresist technology.

In the following examples the abbreviations for the constituents of the stripper mean:

DMI: 1,3-dimethyl-2-imidazolidinone

DMTHP: 1,3-dimethyltetrahydro-2-(1H)-pyrimidinone

AEAE: 2-(2-aminoethylamino)ethanol

AEOE: 2-(2-aminoethoxy)ethanol

TPGME: tripolyleneglycol methyl ether

### Example 1

A commercially available positive photoresist based on diazoquinone/Novolac (Selectilux® P 2100-30, by the E. Merck Co.) was spun at 5000 RPM onto silicon wafers and dried on the hot plate at 100°C for 1 minute. The film thickness was determined at 1.25 µm. Then the coated substrate was secondarily dried in the oven at 200°C for 30 minutes.

The stripping tests were then conducted by immersion in stirred baths of the solvent composition being tested in each case at a temperature of 75°C. After 3 minutes and 6 minutes in each case, the substrates were rinsed with deionized water and the stripping effect on the resist film was evaluated.

Table 1 shows the results: Compositions 1-5 according to the invention are considerably more effective.

**Table 1**

Composition No.		weight%	resist stripping in%	
Component			after 3'	after 6'
1	DMI	/50	95	100
	AEAE	/50		
2	DMI	/60	80	100
	AEAE	/40		
3	DMI	/50	100	100
	3- Amino-1-propanol	/50		
4	DMI	/50	95	100
	3-Amino-2-propanol	/50		
5	DMI	/50	10	90
	AEOE	/50		
VI	DMI	/40	0	10
(reference)	AEAE	/60		
V2	DMI	/70	0	30
(reference)	AEAE	/30		
V3*	TPGME	/49	0	0
(reference)	AEAE	/51		

\*) Composition according to EP 219 789.

### Example 2

The same procedure as an example 1 was used except that the photoresist was secondarily dried for 30 minutes at 150°C, and the stripping tests were performed at room temperature. The time until complete stripping of the resistant was determined for the compositions tested.

Table 2 shows the results: With all of the compositions according to the invention of photoresist was totally removed at room temperature. Composition No. 6 was found to be optimal.

**Table 2**

Composition No.	Component	/weight%	Time for 100% resist stripping
1	DMI	/50	6 minutes
	AEAE	/50	
6	DMI	/52	5 minutes
	AEAE	/48	
7	DMI	/55	7 minutes
	AEAE	/45	
8	DMTHP	/50	20 minutes
	AEAE	/50	

### **Example 3**

Formulation No. 6, which was found to be optimal in example 2, was tested as in example 1. The resist, which had been secondarily dried at 200°C for 30 minutes, was totally removed at a bath temperature of 75°C within 1 minute.

### **Example 4**

A glass plate coated with a thin aluminum film was immersed for 30 minutes in composition No. 6 at 130°C. After being rinsed off with deionized water no attack on the metal film could be noted.

### **Example 5**

A steel plate was coated with a 20 µm thick film of a photo-crosslinkable polyamide acid methacrylate ester formulation (Selectilux®HTR 3 by E. Merck Co.) and dried at 140°C for 30 minutes.

This film could be completely removed by immersion for 5 minutes in a stirred mixture heated at 75°C of 52% DMI and 48% AEAE. (composition No. 6).

### **Example 6**

A silicon wafer was coated with a polyamide acid methacrylate ester formulation (Selectilux® HTR 3, by the E. Merck Co.), dried at 100°C and heat treated for 1 hour at 400°C. The polyimide film thus obtained film had a thickness of 4 µm and could be completely removed by immersion for 15 minutes in a stirred mixture heated at 130°C of 52% DMI and 48% AEAE. (composition No. 6).

## Claims

1. Strippers for photoresists based on
  - (a) an aprotic polar organic solvent and
  - (b) an organic base,

characterized in that they contain as component (a) 45-65 wt.% of at least one of the compounds 1,3-dimethyl-2-imidazolidinone or 1,3-dimethyl tetrahydro-2-(1H)-pyrimidinone and as component (b) 55-35 wt.% of at least one compound of formula I



where X denotes a single bond, O or NH and  $n$ ,  $m$  denote the numbers 1 to 4.

2. Agents as in claim 1, characterized in that they consist of 50-60 wt.% component (a) and 50-40 wt.% component (b).
3. Agents as in claim 1 or 2, characterized in that component (a) is 1, 3-9 ethyl-2-imidazolidinone and component (b) is 2-(2-aminoethylamino) ethanol.
4. Agents as in claim 1, consisting of 52 wt.% 1,3-dimethyl-2-imidazolidinone and 48 wt.% 2-(2-aminoethylamino) ethanol.